Surface-Enhanced Plasmon Splitting in a Liquid-Crystal-Coated Gold Nanoparticle

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We show that, when a gold nanoparticle is coated by a thin layer of nematic liquid crystal, the nanoparticle surface has a strong effect on the director orientation, but, surprisingly, this deformation can enhance the surface plasmon splitting. We consider three plausible liquid crystal director configurations in zero electric field: boojum pair (north-south pole configuration), baseball (tetrahedral), and homogeneous. From the discrete dipole approximation, we find that the surface plasmon splitting is largest for the boojum pair, and this result is in good agreement with experiment.

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Colloidal suspensions and emulsions in anisotropic host media, or coated with anisotropic media such as liquid crystals, have attracted considerable recent interest, since these systems exhibit a novel class of colloidal interactions [1] or the possibility of forming tetravalent binding sites of colloids [2]. The alignment of the principal axis of anisotropic media (known as the director) around a colloidal surface is an important feature; this new colloidal interaction comes from homeotropic alignment, perpendicular to the surface, while tetravalent binding sites come from tangential alignment to the surface.

These systems have also been studied for optical applications [3–6]. For example, related to the emerging nanotechnology, a recent experiment has demonstrated nanoscale control of optical properties on a length scale much less than a light wavelength [5]. The authors observed the surface plasmon splitting of a gold nanoparticle coated with a thin layer of nematic liquid crystal: the surface plasmon resonance frequency in the scattering cross section was shown to depend on the angle between the director and the polarization of incident light. They also showed that, by rotating the director using a static electric field, they could control the change in surface plasmon frequency.

A recent calculation [6] showed that this method could, indeed, produce a measurable change in the surface plasmon frequency, assuming that the director was oriented in the same direction everywhere within the coating or the host media. But in reality, the director field should be influenced near the metal surface [7], and thus the alignment of the liquid crystal director field near the nanoparticle surface may reduce the surface plasmon splitting to hinder some possible applications of this system which involve electrical control of its optical properties. Thus, it is important to investigate quantitatively how an inhomogeneous director field may influence the optical properties of these coated metal particles.

In this Letter, we report on novel optical phenomena arising from the surface deformation (or alignment) of the liquid crystal director field. Our main finding is that this deformation can actually *enhance* this splitting of the surface plasmon frequency. We consider three plausible morphologies for this director field and, using the discrete dipole approximation (DDA) [8,9], compute the deformation-induced splitting of the surface plasmon frequency into two different frequencies polarized parallel and perpendicular to the director. For the expected ''boojum pair'' configuration, the splitting is enhanced, relative to that of a uniform director field, and agrees very well with the measured splitting [5]. The potential importance of this work is discussed below.

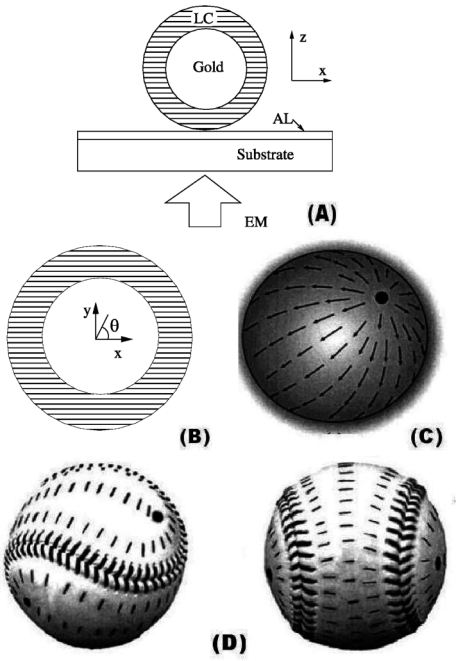

FIG. 1. (a) Schematic of the experimental geometry considered in these calculations. We assume that a spherically coated nanoparticle sits on a substrate. The substrate has a thin coating that aligns the liquid crystal director at the point of contact in the x direction. Monochromatic linearly polarized light (EM) is assumed normally incident as shown. The three possible liquid crystal morphologies which we consider are shown schematically as (b) homogeneous; (c) ''boojum pair''; and (d) ''baseball.'' We calculate the position of the surface plasmon peak as a function of the polarization angle θ indicated in (b).

First, we discuss several possible morphologies for the liquid crystal director field in a nematic liquid crystal layer on a gold nanoparticle. The actual morphology depends strongly on the exact experimental setup. We simply assume that, as illustrated in Fig. 1(a), a spherical coated gold nanoparticle in an air host sits on the substrate, which is coated with a thin alignment layer, so that near the substrate the director will be aligned in the x direction. We also assume that the liquid crystal director is aligned parallel to the surface at both interfaces. This assumption is reasonable: for a metal-liquid crystal boundary, a suitable surface treatment can modify the boundary condition to the tangential boundary condition (director parallel to the surface) [1,10]. Also if the coating is thin, we can assume a tangential boundary condition at the liquid crystal–air interface [11]. Since the anchoring force at the nanoparticle surface can be modified by suitable surface preparation, the director may sometimes satisfy a more general boundary condition, which is not, however, considered in this Letter.

The standard analytical description of liquid crystal morphology is based on the Frank elastic free energy [12]. If there is no external electric field, assuming the tangential boundary condition there are two likely morphologies for a spherical nematic liquid crystal layer on a spherical nanoparticle. For a relatively thick layer, the director field is expected to form a north-south pole-type (or boojum pair) morphology. But, if the nematic liquid crystal layer is very thin so that it can be treated like a two-dimensional surface, the director field is expected to take a baseball-like morphology [2]. These two possibilities are shown in Fig. 1. We calculate the scattering cross section for a liquid-crystal-coated gold nanoparticle, considering both possibilities.

In our actual optical calculation, we have simplified these two morphologies for computational convenience. For the boojum pair morphology, we assume that the director field is everywhere parallel to the surface and points along a latitude between the north and the south poles. This assumption is reasonable because of anchoring, which forces the director field to be everywhere parallel to the particle surface. The liquid crystal director orientation is also affected by the alignment layer in the substrate. If we simply assume a tangential boundary condition where the liquid-crystal-coated nanoparticle touches the substrate, this condition limits the pole positions. For example, in the boojum pair configuration, the alignment layer forces the line between north and south poles to be oriented in the x direction, i.e., parallel to the substrate.

For the baseball morphology, there are four poles, at the vertices of a tetrahedron. Because of the substrate-imposed anchoring, we assume that two of these are located in the lower hemisphere, and that the line between these two poles is parallel to the x axis, while the other two are located in the upper hemisphere, joined by a line parallel to the y axis. To use the DDA, we further simplify this configuration by assuming that the director fields in the lower and upper hemispheres are both homogeneous, and point in the x and y directions, i.e., parallel to the substrate surface in both cases.

To calculate the scattering cross section of the liquid-crystal-coated nanoparticle, we use an approach known as the DDA [8,9]. Given the director fields of the liquid crystal coating, we calculate the scattering cross section C_{scat} of a single nanoparticle as if none of the other particles were present. This amounts to neglecting multiple scattering corrections among the different nanoparticles, consistent with the experiment of Ref. [5]. Also, we ignore the contribution of the substrate to the scattering cross section (although we still include its effects in aligning the liquid crystal director around the nanoparticle as described above). Thus, C_{scat} can be calculated without an orientational average over the scattering object.

As originally formulated, the DDA allows the calculation of properties such as the extinction or scattering coefficient of an irregularly shaped object having a complex, frequency-dependent dielectric constant $\epsilon(\omega)$, embedded in a homogeneous medium of real dielectric constant ϵ_h. In this approximation, the object is taken as an array of point dipoles ($i = 1, \ldots, N$) with dipole moments $\mathbf{P}_i$ and polarizabilities α_i, located at positions $\mathbf{r}_i$. The extension of the DDA to treat an irregularly shaped object which has an anisotropic and spatially inhomogeneous dielectric tensor can be easily done by introducing a position-dependent tensor polarizability $\tilde{\alpha}_i$, and thus the DDA can be applied to our case of a liquid-crystal-coated nanoparticle with a spatially varying director field. Thus $\mathbf{P}_i$ is expressed as

$$\mathbf{P}_i = \tilde{\alpha}_i \mathbf{E}_i, \tag{1}$$

where $\mathbf{E}_i$, the electric field at $\mathbf{r}_i$, is due to the incident wave $\mathbf{E}_{\mathrm{inc},i} = \mathbf{E}_0 \exp(i\mathbf{k}\cdot\mathbf{r}_i - i\omega t)$, plus the contribution of each of the other $N-1$ dipoles:

$$\mathbf{E}_i = \mathbf{E}_{\mathrm{inc},i} - \sum_{j\neq i} \mathbf{A}_{ij}\cdot\mathbf{P}_j. \tag{2}$$

In the DDA, the product $\mathbf{A}_{ij}\cdot\mathbf{P}_j$ can be expressed as

$$\mathbf{A}_{ij}\cdot\mathbf{P}_j = \frac{e^{ikr_{ij}-i\omega t}}{r_{ij}^3}\Big\{k^2\mathbf{r}_{ij}\times(\mathbf{r}_{ij}\times\mathbf{P}_j) + \frac{1-ikr_{ij}}{r_{ij}^2}[r_{ij}^2\mathbf{P}_j - 3\mathbf{r}_{ij}(\mathbf{r}_{ij}\cdot\mathbf{P}_j)]\Big\}. \tag{3}$$

Here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $k = \omega/c \equiv 2\pi/\lambda$, c and λ being the speed of light and wavelength in vacuum. Equations (1)–(3) form a coupled set of $3N$ equations, which can be solved for the N dipole moments $\mathbf{P}_i$ using the complex-conjugate gradient method combined with fast Fourier transforms [8]. Given the $\mathbf{P}_i$'s, C_{scat} for a given coated particle is obtained from the relation

$$C_{\mathrm{scat}} = \frac{4\pi k}{|\mathbf{E}_0|^2}\sum_{i=1}^{N}\left[\frac{2}{3}k^3|\mathbf{P}_i|^2 - \mathrm{Im}(\mathbf{P}_i\cdot\mathbf{E}_{\mathrm{self},i}^*)\right], \tag{4}$$

where $\mathbf{E}_{\mathrm{self},i} = \mathbf{E}_i - \mathbf{E}_{\mathrm{inc},i}$.

Now we discuss the relation between the local polarizability tensor $\tilde{\alpha}$ of these point objects and the local dielectric tensor $\tilde{\epsilon}(\omega)$. To carry out the above calculation, one needs an expression for the polarizability tensor $\tilde{\alpha}$. For a material with an *isotropic* scalar dielectric function $\epsilon(\omega)$, one simple means of connecting a scalar polarizability α to ϵ is the Clausius-Mossotti relation. This relation can be easily generalized to an anisotropic medium by replacing the scalar dielectric function and other scalar variables by a dielectric tensor and other tensor variables [13]. Thus, we can generalize the lattice dispersion relation [9], used to connect α to ϵ in the isotropic case, to the anisotropic case. To obtain the position-dependent anisotropic polarizability tensor $\tilde{\alpha}$, we insert the position-dependent anisotropic dielectric tensor into this generalized lattice dispersion relation.

To apply this approach to the liquid crystal morphologies discussed above, we need to transform the local dielectric tensor from a frame of reference in which it is diagonal (the ''diagonal frame'') into the laboratory frame, using a suitable similarity transformation. In practice, this transformation is not difficult, since the local $\tilde{\epsilon}$ and $\tilde{\alpha}$ are simultaneously diagonalizable. In practice, we find that to calculate a given diagonal element of the lattice dispersion relation polarizability, we need only the same diagonal element of the dielectric tensor. Thus, the diagonal polarizability tensor using the lattice dispersion relation can be calculated in this diagonal frame. Also, the lattice dispersion relation is invariant under the above similarity transformation. Thus, if the dielectric tensor is initially diagonal in some frame of reference, we can obtain the diagonal polarizability using lattice dispersion relation in this frame first, then carry out a suitable similarity transformation on this diagonal polarizability to get the polarizability in the laboratory frame.

To check the convergence of our DDA calculation, we considered a liquid-crystal-coated nanoparticle with a gold radius of 30 nm, surrounded by a nematic liquid crystal of 30 nm thickness. We carried out the DDA calculations with a variable number of point objects representing the liquid-crystal-coated gold nanoparticle. This was accomplished by varying the ''linear mesh size'' $M \equiv 2R/d$, where d is the distance between adjacent point objects on a simple cubic mesh, and R is the radius of a metal nanoparticle, i.e., 30 nm in this case. In Fig. 2(a), we plot the scattering cross section as a function of this linear mesh size. As can be seen, the peak position converges well with increasing linear mesh size M, but its height converges less well. We observe the same behavior in the case of a nanoparticle with a Drude dielectric constant without an liquid crystal coating layer embedded in a homogeneous medium as shown in Fig. 2(b). Compared with the exact Mie theory, the peak position converges well even in the case of $M = 20$, while its height converges more slowly (within about 5% in the case of $M = 120$). In Fig. 2, we use Drude dielectric function with $\omega_P \tau = 7.7$. Thus, our DDA results for the *position* of the surface plasmon peak from a liquid-crystal-coated nanoparticle are robust against changes of the linear mesh size, even if we consider scattering from position-dependent anisotropic media. Hence, we can calculate the positions of the scattering peaks with and without a liquid crystal coating, and for various coating thicknesses, using the DDA, and compare the results to measurements of Ref. [5].

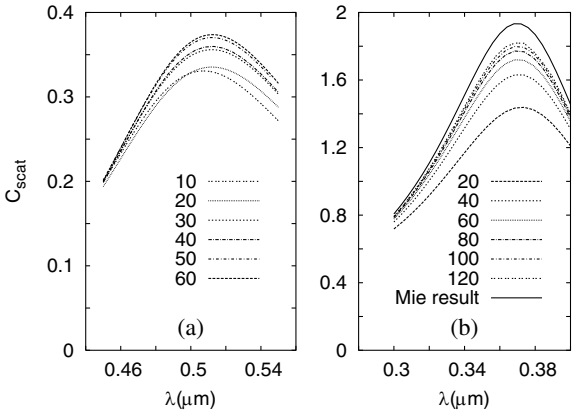

FIG. 2. Calculated scattering cross section versus wavelength λ for (a) a liquid-crystal-coated metal nanoparticle at angle $\theta = 0°$ for boojum pair configuration with radius 30 nm, liquid crystal coating thickness 30 nm, and varying the DDA mesh size, as indicated in the legend; (b) same for a bare metal nanoparticle and a radius 30 nm in an air host with various mesh sizes. Solid line indicates the exact Mie result. Here we used Drude dielectric function, for simplicity.

As a first calculation with the actual gold dielectric function, we studied how the surface plasmon peak position changes as a function of liquid crystal layer thickness, under the assumption that the director field is uniformly oriented in one direction parallel to the substrate. Here for the dielectric function of a gold nanoparticle, we used a finite-particle-size corrected dielectric function, which we can estimate from the tabulated values of bulk gold [14]. In this case, we calculated the scattering cross section for an incident electric field polarized parallel to the liquid crystal director, i.e., $\theta = 0°$ in Fig. 1(b). By comparing the position of this calculated surface plasmon peak to that measured in Ref. [5], using a similar setup, we estimate that the thickness of the liquid crystal layer in those measurements is $\sim$30 nm, comparable to the radius of the gold particle.

In Fig. 3, we plot the position of the plasmon peak versus the polarization angle of the incident light, for three liquid crystal coating morphologies. Two of the morphologies are the ''boojum pair'' and ''baseball'' configurations described above, and the third is a director uniformly oriented in one direction parallel to the substrate. A morphology with two singular points of the north-south pole-type shows the biggest peak shift (about 0.023 eV) with a change in the polarization angle; the magnitude of this shift makes the best fit to the value ($\sim$0.030 eV) observed in the experiments. By contrast, the value obtained when we assume a uniform director field is about 0.011 eV, and that obtained for the baseball-like geometry is the smallest

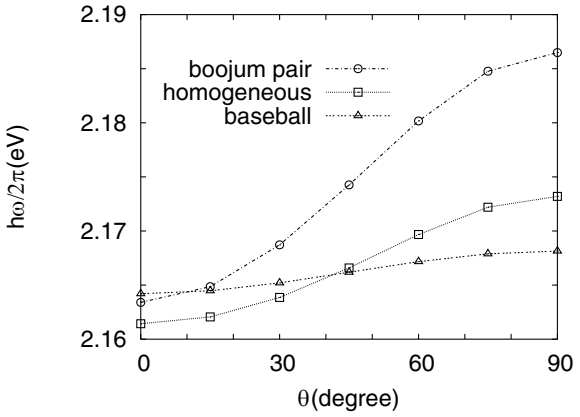

FIG. 3. Frequency of peak in scattering cross section for a liquid-crystal-coated gold nanoparticle (with the actual gold dielectric function with finite-particle-size correction) versus angle θ, for boojum pair, homogeneous, and baseball configurations.

among the three different morphologies ($\sim$0.004 eV). Thus, the surface deformation of the director field, which is caused by the gold nanoparticle surface and by the boundaries with host medium or the substrate, can strongly influence and even enhance the plasmon splitting of this system. This enhancement suggests that the optical properties of such nanoscale systems can be controlled electrically, by inclusion of liquid crystals.

The present calculations suggest that the liquid crystal film in the experiments [5] is probably relatively thick ($\sim$30 nm). If the coating were thinner, the stronger surface perturbation might lead to a baseball-like configuration as suggested in Ref. [2], and hence, a much smaller surface plasmon splitting than seen in the experiments. We speculate that there may be a boojum pair–baseball crossover as the film gets thinner. If so, monitoring the splitting as a function of liquid crystal coating thickness would provide an optical signature of such a crossover. Moreover, if there is a strong suppression of the plasmon splitting, as we find in the case of a baseball-like configuration, this would be an experimental indication that the coating thickness is suitable for forming tetravalent functionalized points around the gold nanoparticles, which can realize a tetravalent chemistry of colloids [2].

Finally, we briefly discuss a liquid-crystal-coated gold nanoparticle in an applied electric field. If we assume the tangential boundary condition, two boojum defects are induced on the surface of the nanoparticle [7]. In this case, the morphology of liquid crystal director near the surface of the gold nanoparticle, will be the same as the boojum pair case in the zero applied electric field, and thus we expect that the splitting of the peak in the scattering cross section should have the same enhancement by surface deformation as in the zero applied field. The effects of an electric field, and more general boundary conditions, may need further investigation.

The present results may have a wide range of applications in nanoscience and nanotechnology, because they show that optical properties of systems containing nanoparticles can be sensitively controlled with the use of liquid crystals. The transmission and absorption of such materials could be tuned by a dc electric field, which will alter the liquid crystal director field, or by controlling the surface interactions between metal and liquid crystal. This opens up the possibility of new classes of tunable electro-optic materials based on nanoscale metallic particles combined with liquid crystals. Moreover, the desirable boojum pair configuration may form by self-organization, thereby allowing new types of self-assembled nano-optical devices. Finally, a tetrahedral baseball-like director configuration is a potential building block for a self-assembled three-dimensional photonic crystal with a diamond structure. The measured surface plasmon splitting may be a valuable diagnostic to determine when this baseball configuration forms.

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